

Soap-Based Detergent Formulations: XXIII. **4253**

Synthesis of p-Sulfobenzyl Ammonium Inner Salts and
Structural Correlation with Analogous Amphoteric¹

Soap-Based Detergent Formulations: XXIII. Synthesis of p-Sulfobenzyl Ammonium Inner Salts and Structural Correlation with Analogous Amphoterics¹

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ABSTRACT AND SUMMARY

Two series of p-sulfobenzyl ammonium inner salts, $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_4\text{SO}_3^-$ and $\text{RCONH}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_4\text{SO}_3^-$, where R is a straight chain alkyl group, were prepared by sulfonation of the corresponding quaternary ammonium chlorides. Although both series have excellent lime soap dispersion properties, the former series gave optimum detergency at considerably shorter alkyl chain length than the latter series. The detergency, lime soap dispersion ability, and solubility of these compounds were compared with those of structurally analogous aliphatic sulfobetaines. Structural variations, such as length and nature of the bridge between the cationic and anionic groups, length of the lipophilic chain, and insertion of an amidopropyl group into the lipophilic portion of the molecule, significantly altered the detergency and solubility but not the lime soap dispersing ability of the amphoterics.

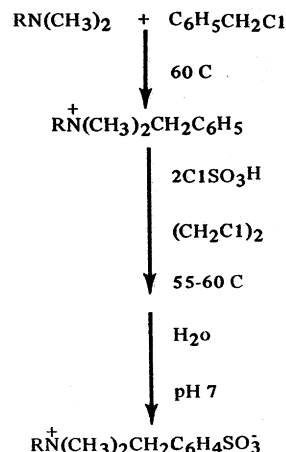
INTRODUCTION

In the course of an ongoing study of soap-based detergents, amphoteric surfactants have been found to be effective lime soap dispersing agents (LSDA) and comparable to or better than a high-phosphate control in detergency performance when formulated with tallow soap and a silicate builder (1-3). Specifically, amphoterics bearing a quaternary ammonium nitrogen and a terminal sulfonate group of the general structure, $\text{RN}^+(\text{CH}_3)_2\text{C}_n\text{H}_{2n}\text{SO}_3^-$, where R is a long alkyl chain and n an integer from 2 to 4, have shown outstanding surface active properties. The introduction of an amido group to give amphoterics of the structure, $\text{RCONHCH}_2\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{C}_n\text{H}_{2n}\text{SO}_3^-$, further enhances the lime soap dispersing ability and improves water solubility (lowers the Krafft point) (1,2).

In this study we investigated sulfobenzyl ammonium inner salts, which differ from the previously mentioned sulfobetaines in that a benzyl linkage bridges the quaternary nitrogen and sulfonate group rather than a two-carbon, three-carbon, or four-carbon aliphatic linkage. Two series of sulfobenzyl compounds were prepared, the para-sulfonated benzalkonium compounds of the general structure, $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_4\text{SO}_3^-$, where R = an even number carbon chain from C_{12} to C_{18} , and the analogous amido amphoterics of the general structure, $\text{RCONHCH}_2\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{C}_6\text{H}_4\text{SO}_3^-$, where R = an odd number carbon chain from C_{11} to C_{17} . The former compounds had been previously reported by Piggott (4), whereas the latter, to the best of our knowledge, are novel amphoteric surfactants.

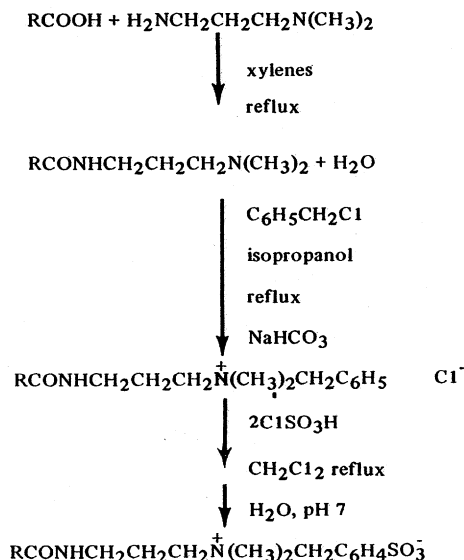
The synthesis of the p-sulfobenzyl amphoterics offers some advantages over the synthesis of the three-carbon and four-carbon bridge sulfobetaines, which were prepared from

potentially carcinogenic (5) and currently commercially unavailable propanesultone or butanesultone, respectively (6). The synthesis of the alkyl p-sulfobenzyl series is an industrially feasible procedure employing the direct sulfonation of commercially available benzalkonium chlorides with either sulfur trioxide or chlorosulfonic acid (see Scheme 1). The amido p-sulfobenzyl compounds were obtained by a three-step synthesis involving, initially the formation of fatty amide according to the procedure of Muzyczko et al. (7), followed by the conventional quaternization with benzyl chloride. The resulting quaternary ammonium



Scheme 1

chlorides were then sulfonated directly with chlorosulfonic acid (see Scheme 2).



Scheme 2

¹Presented at the AOCS Meeting, Chicago, September 1976.

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TABLE I
Conditions for the Preparation of $C_{12}H_{25}N^+(CH_3)_2CH_2C_6H_4SO_3^-$

Run number	Sulfonating agent	Sulfonation temperature, C	Reaction time (hr) ^a	Solvent	Yield (%)
1	CISO ₃ H	ambient	24	(C ₁ H ₂) ₂	30
2	CISO ₃ H	52	17	(C ₁ H ₂) ₂	62
3	CISO ₃ H	84	17	(C ₁ H ₂) ₂	poor
4	CISO ₃ H	58	23	distilled (C ₁ H ₂) ₂	85
5	CISO ₃ H	57	25	distilled (C ₁ H ₂) ₂	90
6	SO ₃	ambient	1-2	(C ₁ H ₂) ₂	0
7	SO ₃	50	1-2	(C ₁ H ₂) ₂	68
8	SO ₃	40	1-2	CH ₂ Cl ₂	68
9	SO ₃	40	1-2	CH ₂ Cl ₂ ^b	<50
10	SO ₃	52	1-2	(CH ₂ Cl) ₂	82

^aNo further reaction after time indicated.

^bOne-half volume of solvent used in run No. 1 to 8.

A comparison of solubility behavior, lime soap dispersing ability, and detergency of the sulfobenzyl compounds of this study with those of the previously reported amphoteric analogs offers insight into the effect of structural variations on surface active properties.

EXPERIMENTAL PROCEDURES

Materials

Lauric, myristic, palmitic, and stearic acids were obtained from Ashland Chemical Company (Columbus, OH) and were either distilled or recrystallized to 99% purity by GLC. Armak Chemical Division, Akzona, Incorporated (Chicago, IL) supplied N,N-dimethyldodecylamine (Armeen DM12D), N,N-dimethyltetradecylamine (Armeen DM14D), N,N-dimethylhexadecylamine (Armeen DM16D), and N,N-dimethyloctadecylamine (DM18D), which were obtained in >99% purity (GLC) by fractional distillation. N,N-Dimethyl-1,3-propanediamine ("Dimethylaminopropylamine") was obtained through the courtesy of Jefferson Chemical Company, Incorporated (Houston, TX). Benzyl chloride was obtained from Eastman Chemical Company (Rochester, NY) and vacuum distilled before use. Chlorosulfonic acid was supplied by Matheson, Coleman, and Bell (Norwood, OH). Liquid sulfur trioxide was the product of Allied Chemical Company (New York, NY). Fabrics for detergency evaluations were obtained from Testfabrics, Incorporated (Middlesex, NJ) (EMPA and TF) and U.S. Testing, Incorporated (Hoboken, NJ) (UST).

Dichloromethane and 1,2-dichloroethane were purified and dried according to literature methods, and nanograde isopropanol was used without further purification.

Synthesis of Quaternary Ammonium Chlorides

A variation of the procedure of Piggott (4) was utilized to prepare these compounds. Typically, a 100-ml, 3-neck, round-bottom flask, equipped with condenser, drying tube, thermometer, magnetic stirrer, and heating mantle, was charged with 14.1 g (0.11 mole) of benzyl chloride and 0.074 mole of the appropriate tertiary amine. The reactants were heated for 4 to 6 hr. The reaction temperature was varied with the chain length of the amine (e.g., N,N-dimethyl-N-dodecylamine, 60 C; N,N-dimethyl-N-hexadecylamine, 105 C) since the longer the alkyl chain, the higher the reaction temperature required to prevent solidification of the reaction product as it formed. The final reaction mixture, a white solid at room temperature, was dissolved in 75 ml of 95% methanol and extracted with petroleum ether (2 x 20 ml). After the aqueous methanol had been stripped off, the resulting viscous mass was dried by azeotropic distillation with toluene and finally was vacuum

dried at room temperature. The crude reaction product, a bright white solid, was recrystallized from acetone in nearly quantitative yields.

Sulfobenzyl Ammonium Inner Salts

CISO₃H sulfonation: A 250-ml, 3-neck, round-bottom flask, equipped with water condenser and drying tube, magnetic stirrer, thermometer, and nitrogen inlet, was charged with 0.029 mole of the appropriate alkyl dimethylbenzylammonium chloride and 115 ml distilled 1,2-dichloroethane. Chlorosulfonic acid (6.98 g; 0.06 mole) was pipetted in one portion into the reaction flask, and the reaction temperature was maintained at 55-58 C for 20-24 hr. The reaction mixture was cooled in an ice bath and quenched by small additions of distilled water. The solution was transferred to a separatory funnel (500 ml), and three distinct layers were visible. The bottom organic layer was removed and discarded. The aqueous layer and dark brown middle layer were neutralized to pH 7 with small additions of 25% NaOH (0.1 N NaOH used near pH 7). The neutralized solution formed two layers; the aqueous layer contained some surfactant and mostly inorganic salts while the dark viscous bottom layer contained only reaction product. The solvent was removed from the neutralized bottom layer by high speed rotary evaporation, and a viscous oil resulted. The p-sulfobenzyl compound was triturated with acetone and separated as an off-white solid. The crude products were recrystallized from absolute ethanol.

SO₃ sulfonation: Typically, a 250-ml, 3-neck, round-bottom flask containing 120 ml of undistilled 1,2-dichloroethane was equipped with a distillation trap, condenser, and drying tube. Water (impurity) was removed by azeotropic distillation of solvent, and the remaining dry solvent was allowed to come to room temperature (under nitrogen). Then, the round-bottom flask was equipped with a reflux condenser, drying tube, magnetic stirrer, and heating mantle, and 10 g (0.029 mole) of N-benzyl-N,N-dimethyldodecylammonium chloride was added. A separate round-bottom flask containing liquid SO₃ was attached to the main reaction flask with a U-shaped connecting tube having a side hose connector (for drying tube) and a long drip tip which extended into the reaction solution. Liquid SO₃ (6.0 g; 0.075 mole) was warmed with a heat gun and distilled under a positive pressure of nitrogen into the main reaction flask. The reaction solution was maintained at 60-70 C during addition (0.5 to 0.75 hr). After addition of sulfur trioxide, the reaction temperature was lowered and maintained at 52 C for 2 hr. The dark brown, viscous reaction mixture was chilled in an ice bath, quenched with 75-100 ml of H₂O, and neutralized to pH 7. When the mixture was transferred to a separatory funnel, three layers

TABLE II
Data for Sulfobenzyl Amphoteric Surfactants

Compound	Detergency ΔR%						Yield ^f (%)	LSDR ^g	Krafft point ^h
	0.2% Binary formulation ^a			0.2% Ternary formulation ^b					
	EMPA ^c	UST ^d	TF ^e	EMPA	UST	TF			
⁺ RN(CH ₃) ₂ CH ₂ CH ₆ H ₄ SO ₃ ⁻									
R = C ₁₂ H ₂₅	80	144	105	103	78	97	50	3	>99
C ₁₄ H ₂₉	67	100	95	93	44	76	27	3	>99
C ₁₆ H ₃₃	40	44	37	50	22	37	40	4	>99
C ₁₈ H ₃₇	33	44	21	47	-22	21	45	4	>99
⁺ RCONH(CH ₂) ₃ N(CH ₃) ₂ CH ₂ C ₆ H ₄ SO ₃ ⁻									
R = C ₁ H ₂₃	76	88	88	97	75	85	47	3	>99
C ₁₃ H ₂₇	69	138	93	83	88	83	66	2	>99
C ₁₅ H ₃₁	52	163	90	90	125	78	48	3	>99
C ₁₇ H ₃₅	45	138	98	66	138	65	45	3	>99
Control				100	100	100			

^aBinary = 75% tallow soap and 25% amphoteric surfactant.

^bTernary = 65% tallow soap, 20% amphoteric surfactant, and 15% sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2 = 1:1.6$).

^cEMPA = EMPA 101 cotton.

^dUST = U.S. Testing Company cotton.

^eTF = Testfabrics polyester-cotton blend with permanent press finish.

^fFirst crop from absolute ethanol crystallization.

^gThe number of grams of agent (LSDA) required to prevent precipitation of 100 g of sodium oleate in hard (333 ppm- 60% Ca^{+2} , 40% Mg^{+2}) water (8).

^hSee reference 9.

were visible. Since the top aqueous layer and the bottom organic layer contained very little sulfonated product by infrared spectroscopy, only the middle dark brown, viscous layer was retained, and the product was triturated with acetone and separated as an off-white solid.

The alkyl sulfobenzyl ammonium inner salts were previously reported by Piggott (4) as gelatinous masses; however, the products of the two preceding sulfonation procedures were obtained as white crystalline solids. Some variations of the sulfonation procedures are illustrated in Table I and are discussed later. The surface active properties and yields of the alkyl p-sulfobenzyl ammonium inner salts are reported in Table II.

Amidoamines

The fatty amides of N,N-dimethylaminopropylamine were prepared from their corresponding fatty acids according to the procedure of Muzyczko et al. (7), except that xylene was utilized as solvent instead of toluene.

Quaternary Amidoammonium Chlorides

A variation of the method of Muzyczko et al. (7) was utilized to prepare this series of compounds. A 2-liter, 3-neck, round-bottom flask, equipped with a reflux condenser, drying tube, thermometer, magnetic stirrer, and heating mantle, was charged with 0.135 mole of the appropriate amide, 9.07 g (0.108 mole) of sodium bicarbonate, 25.2 g (0.2 mole) of benzyl chloride, and 500 ml isopropanol. The reaction solution was allowed to reflux gently for 6 hr. Completion of the reaction was determined by free amine titration (~0% amine). The reaction mixture was filtered, stripped, and vacuum dried. The resulting white solids were recrystallized from acetone in an 85-90% yield.

Sulfobenzyl Amidoammonium Inner Salts

A 500-ml, 3-neck, round-bottom flask was equipped with reflux condenser, drying tube, nitrogen inlet, heating mantle, and magnetic stirrer. The appropriate amidoam-

monium chloride (0.073 mole) was dissolved in 275 ml distilled methylene chloride, and 18.7 g (0.16 mole) of chlorosulfonic acid was added slowly into the reaction solution at room temperature. The reaction mixture was allowed to reflux gently for 24 hr and chilled in an ice bath before quenching by the slow addition of distilled water (~100 ml). The reaction mixture was transferred to a separatory funnel, and the bottom organic layer was removed and discarded. The aqueous layer, which contained a viscous, gelatinous, unfilterable mass, was neutralized to pH 7 with 25% NaOH (0.1% near pH 7), stripped by high-speed rotary evaporation, and dried in vacuo. The solid was suspended in boiling absolute ethanol (1.5 liter) and the insoluble inorganic salts were filtered off and discarded. When the ethanol was removed, a straw-colored solid was obtained in 90-95% yield for each of the amido p-sulfobenzyl derivatives, and the first crops from recrystallization in absolute ethanol resulted in 45-65% yields of pure compounds (see Table II).

Instrumental Analyses

Infrared spectra were obtained on a Perkin Elmer 237B Spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Jeolco C60H instrument.

Surface Active Properties

Lime soap dispersing requirements: LSDR were obtained by the Borghetty-Bergman procedure (8). While the sulfobenzyl amphoteric are not water soluble, they were all solubilized in combination with sodium oleate. Results are given in Table II.

Krafft points (9): All amphoteric had Krafft points >99°C (see Table II).

Detergency evaluations: All washings were run in a Tergotometer for 20 min at 120 F in 1 liter of 300 ppm hardness water with an agitation speed of 100 cpm. Five circular swatches each (4 in. diameter) of EMPA 101 cotton, U.S. Testing cotton (UST), and Testfabric cotton-

polyester with permanent press finish (TF) were washed together in each beaker. Binary formulations (75% tallow soap and 25% amphoteric surfactant) and ternary formulations (65% tallow soap, 20% amphoteric surfactant, and 15% sodium silicate, $\text{Na}_2\text{O}:\text{SiO}_2 = 1:1.6$) were prepared with each sample. Detergency ($\Delta R\%$) is reported in terms of reflectance as follows:

$$\Delta R = R_{\text{after}} - R_{\text{before}}$$

$$\text{Percent detergency} = \frac{\Delta R_{\text{test}}}{\Delta R_{\text{control}}} \times 100$$

The commercial 50% phosphate control detergent was run separately with each series. Results are reported in Table II.

RESULTS AND DISCUSSION

Synthesis

The synthetic route (Scheme 1) previously mentioned for the preparation of the alkyl p-sulfobenzyl ammonium inner salts is straightforward. The quaternary ammonium chlorides are available commercially as a mixture of homologs; however, we were interested in determining the surface active properties of individual homologs, hence each of the benzalkonium chlorides was synthesized separately for this study. The conditions for the preparation of N,N-dimethyl-N-dodecyl-N-(p-sulfobenzyl) ammonium inner salt with either chlorosulfonic acid or sulfur trioxide as sulfonating agent were investigated (Table I). The reaction progress was followed by IR and by a modification of the Cahn (10) cationic titration (1,2). Two moles of chlorosulfonic acid were needed to form the sulfonyl chloride, which hydrolyzed readily in water to the sulfonic acid, whereas only one mole of sulfur trioxide was required to yield the sulfonic acid. Time, temperature, and solvent affected the reaction yields. In general, at least 17 hr were required for complete reaction with chlorosulfonic acid, while with sulfur trioxide, sulfonation was instantaneous. The optimum sulfonation reaction temperature seemed to fall between 50-60 C; therefore, 1,2-dichloroethane, rather than methylene chloride, was the solvent of choice. In addition, although water was azeotroped from 1,2-dichloroethane before use for all reactions, better yields resulted when the solvent was also distilled to remove higher boiling impurities (Table I, entries 4 and 5). These higher boiling impurities in 1,2-dichloroethane are known to react with sulfonating agent (11) while 1,2-dichloroethane itself does not (12).

The amido p-sulfobenzyl ammonium inner salts were synthesized as previously mentioned (Scheme 2). The sulfonation proceeded in excellent yield in refluxing methylene chloride without accompanying sulfamation. Amides are known to produce sulfamates (i.e., $\text{RCON}(\text{SO}_3\text{Na})\text{R}$) when reacted with chlorosulfonic acid in pyridine (13). Probably, the sulfamate does not form under acidic reaction conditions because the amide nitrogen is unreactive toward electrophilic attack of SO_3 .

Both types of p-sulfobenzyl amphoterics had IR and NMR spectra, as well as elemental analyses, in agreement with their assigned structures. Specifically, their NMR spectra confirmed sulfonation in the para position exclusively.

Surface Active Properties

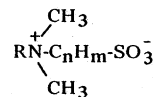
Comparison of benzyl sulfobetaines: The surface active property data (LSDR, Krafft points, and detergency) for both types of benzyl sulfobetaines are shown in Table II. The LSDR values of the benzyl sulfobetaines of this study fall in the same range as those for nearly all the sulfo-

betaines studied in this laboratory (1-3). As was observed previously for analogous amphoterics (1,2), introduction of an amido group into the molecule results in a slight lowering of the LSDR. Although introduction of an amido group does not lower the Krafft points of these sulfobenzyl compounds, an improvement in detergency performance is observed. The amido p-sulfobenzyl amphoterics are more soluble than the alkyl p-sulfobenzyl derivatives, when combined with soap.

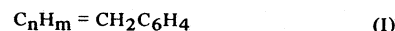
The detergency performance of the alkyl homologs peaks at C_{12} (which has detergency comparable to the high-phosphate control) but diminishes rapidly as the alkyl chain is lengthened. Extrapolation of these data suggests that the shorter chain homologs ($R < \text{C}_{12}$) should exhibit improved detergency relative to the C_{12} . The shorter chain homologs were not prepared because of the unavailability of starting materials (i.e., C_8 and C_{10} amines).

With few exceptions, the detergency performance of the formulations with the amido benzyl sulfobetaines is comparable to the high-phosphate control and changes only slightly over the C_{11} to C_{17} range studied. In general, the detergency performance of both series is quite similar at shorter alkyl chain length (C_{12}) but diverges as the lipophilic chain is lengthened. Overall, the amido p-sulfobenzyl series outperforms the alkyl p-sulfobenzyl compounds in lime soap dispersing ability and detergency.

Comparison of benzyl and aliphatic sulfobetaines: It is interesting to compare the surface active properties of sulfobetaines that vary only in the bridge between the quaternary nitrogen and sulfonate group. The benzyl (I) sulfobetaines, reported in this paper, are illustrated below, as well as two-carbon (II), three-carbon (III), and four-carbon (IV) bridge sulfobetaines, studied previously by Parris et al. (1,2). When R is an alkyl group, the LSDR values for the benzyl (I) and aliphatic sulfobetaines (II-IV)



$R = \text{C}_{12}\text{H}_{25}, \text{C}_{14}\text{H}_{29}, \text{C}_{16}\text{H}_{33}, \text{C}_{18}\text{H}_{37}, \text{or } \text{C}_{15}\text{H}_{31}\text{CONHC}_3\text{H}_6$



are quite similar, the majority ranging from 2 to 4. However, the Krafft points range from <0 to >99 C. The increase in Krafft point is four-carbon (0 C) \sim three-carbon \gg two-carbon $>$ benzyl (99 C) bridge and parallels the improvement in detergency performance, displayed in Figure 1. In the figure the detergency performance for series I-IV ($R = \text{alkyl}$) is plotted vs. lipophilic chain. For clarity, only UST fabric is represented, but the EMPA and TF fabrics also show similar trends. The benzyl (I) and two-carbon bridge (II) derivatives display a similar pattern of decreasing detergency performance with increasing alkyl chain length while the three-carbon (III) and four-carbon bridge (IV) analogs display detergency performance equal or superior to the high-phosphate control. With the exception of IV for which C_{12} or C_{14} homolog data are unavailable, the detergency for series I-IV is similar at shorter alkyl chain lengths but diverges as the chain is lengthened. The three-carbon (III) and four-carbon (IV) bridge sulfobetaines in the range of alkyl chain lengths studied appear less sensitive than their benzyl and two-carbon bridge analogs to an increase in the lipophilicity of the molecule.

When the alkyl chain is replaced with a palmitamido-propyl group ($R = \text{C}_{15}\text{H}_{31}\text{CONHC}_3\text{H}_6$), the LSDR values improve slightly and the Krafft points for series II-IV de-

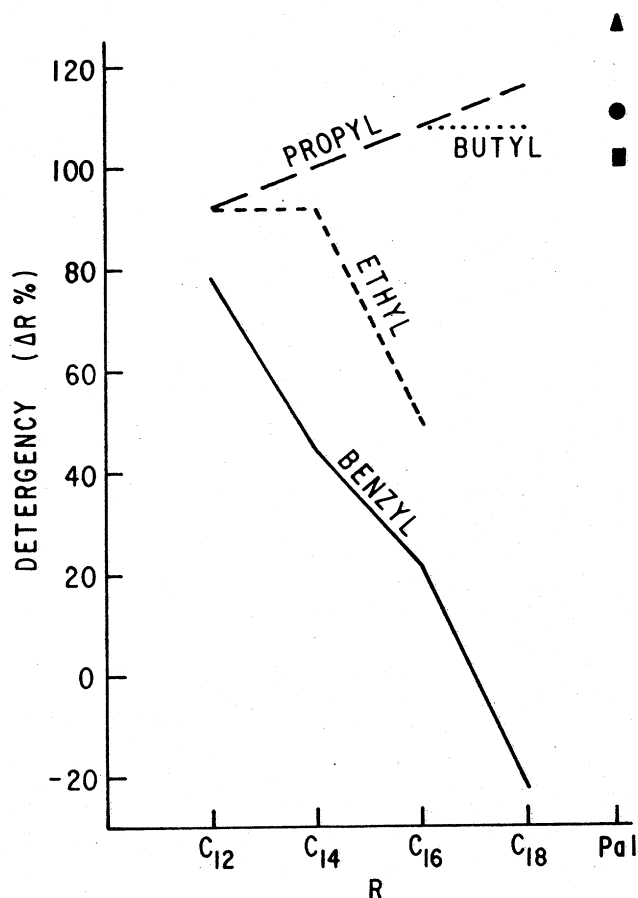


FIG. 1. Relative detergency ($\Delta R\%$) for ternary formulation of sulfobetaines ($RN(CH_3)_2C_nH_mSO_3^-$) vs. lipophilic chain length (R) for UST fabric. All samples are standardized to a leading high-phosphate detergent (control = 100%). For R = alkyl (C_{12} to C_{18}), C_nH_m = benzyl (—), ethyl (---), propyl (— —), and butyl (.....). For R = Pal ($C_{15}H_{31}CONHC_3H_6$), C_nH_m = $CH_2C_6H_4$ (Δ), C_2H_4 (\bullet), C_3H_6 (\blacksquare), and C_4H_8 (\blacklozenge). The ethyl and butyl palmitamidopropyl derivatives (\bullet) gave the same detergency performance.

crease (1,2) while the benzyl (I) compound remains insoluble. However, Figure 1 clearly shows that all the palmitamidopropyl derivatives (I to IV) have detergency performance comparable to that observed for the three-carbon (III) and four-carbon (IV) bridge sulfobetaines (R = alkyl). This suggests that the solubility of the amphoteric in combination with soap, rather than a low Krafft point, is essential for good detergency. This mutual solubilization effect of soap and amphoteric has been reported by Weil et al. (14).

When the existing data are collated, it appears that:

1. The benzyl (I) and two-carbon bridge (II) sulfobetaines (R = alkyl) show similar but poorer surface active properties (except LSDR) than their three-carbon (III) and four-carbon (IV) bridge analogs, and they (I and II) show a similar improvement in surface active properties when R is $C_{15}H_{31}CONHC_3H_6$.

2. For sulfobetaines I-IV (R = alkyl) there is (a) a correlation between detergency and solubility; (b) no correlation between detergency and bridge length (between anionic and cationic sites) if the benzyl derivative is included.

3. A minimum separation of at least 4 atoms between the positively charged quaternary nitrogen and the negatively charged sulfo or amido oxygen (i.e., δ^- O δ^+ N) is necessary for good detergency.

4. There is no overall correlation between Krafft point or LSDR values and detergency performance.

We are now led to believe that the charge separation and flexibility of the head groups influence the surface active properties of these sulfobetaines profoundly and probably govern intramolecular ion pair formation and/or soap-amphoteric association.

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